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Phosphorus Fractions in Soils of East Baton Rouge Parish.

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PHOSPHORUS FRACTIONS
IN
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ABSTRACT

Total, inorganic and organic phosphorus (P) were determined in 47 soil samples selected from East Baton Rouge Parish. Selective dissolution analysis was applied to fractionate the inorganic P compounds. Other determinations included were per cent of total nitrogen, per cent of clay, and pH.

Organic P averaged 159 ppm in surface soil samples and 38 ppm in subsoils. As a percentage of the total P, organic P averaged 54.2 per cent for the surface soils and 21.0 per cent for the subsoils. Statistical correlations of organic P with total P ($r^2 = 0.74$) and with total nitrogen ($r^2 = 0.57$) were positive and highly significant. Organic P was positively correlated with pH but the correlation coefficient was of low magnitude.

Linear and multiple correlations were determined between and among data for three soil tests for "available" P, five inorganic P fractions, pH and clay content.

$NaHCO_3$-extractable P was positively correlated with each of the five inorganic soluble P fractions (Al phosphates, Fe phosphates, Ca phosphates and occluded Al and Fe phosphates) and negatively correlated with pH and clay content. The highest simple correlation coefficient was that with Al-phosphate ($r^2 = 0.896$); whereas occluded Al-phosphate and pH gave low correlation coefficients when associated with $NaHCO_3$-extractable P as dependent variable. Multiple linear correlations were computed in which non significant independent variables were dropped. The correlation coefficient R^2 decreased only from 0.91 to 0.90 when all variables except Al-phosphate were excluded.

The P extracted by ammonium acetate solution (pH 4.2) was positively correlated with each of four inorganic soluble P variables and negatively correlated with occluded Al-phosphate, pH and clay content. The highest simple correlation coefficient was again that with Al-phosphate (r^2 =0.873). In a multiple linear correlation analysis ammonium acetate-P was correlated only with Al-phosphate to a highly significant degree. R^2 was reduced from 0.90 to 0.87 when all other independent variables were excluded.

The P extracted by the Bray reagent was positively correlated with all the inorganic P fractions and pH, and negatively correlated with clay content. The highest correlation coefficient related Bray extractable P to Al-phosphate, (r^2 = 0.914). In a multiple correlation considering all the independent variables R^2 was 0.947. R^2 decreased from 0.947 to 0.914 when all variables except the Al-phosphate were dropped from the function. The R^2 was 0.930 when the other significant variable Ca-phosphate was also included.

INTRODUCTION

Although most of the soil phosphorus (P) tests in common use today for measuring P "available" to the plant were developed empirically rather than from an estimation of the P-fractions which are related to "availability", their principal objective has been a practical one: to estimate the P fertility level of soils. Such estimates were used for predicting the fertilizer needs for crops to be grown in a certain area.

Current ideas on this subject emphasize, however, that a soil test should provide basically the quantitative measure of the degree to which each of the soil P-fractions are related to plant availability, taking in account that relative amounts of soil P compounds present in any soil vary because of weathering, pH, organic matter content, parent material, cropping, and fertilizer practice; that soil P, as a first step, may be broadly classified into organic and inorganic forms; and that inorganic forms are usually more related to plant "availability", and they may be grouped, when subjected to selective dissolution analysis, into the chemical forms - aluminum, iron, and calcium phosphates, and occluded iron-aluminum-phosphates.

Since the total amounts of the different soil P-forms, in these more complete studies, can be estimated separately, it is reasonable to expect that their relationship to plant phosphorus "availability" may be used as a basic criteria for P soil test development.

It has been also stressed that considerable research directed toward characterizing and evaluating organic P in soils, indicates that organic P reactions play a vital part in the overall economy of soil P for plant growth.

In this approach there has been a gradual development in procedures for fractionating the inorganic soil P. In some early works the P procedure was divided into acid-soluble inorganic P and alkali-soluble inorganic and organic fractions. Other investigators used solubility curves in which the soil was extracted with solutions of varying pH. The comparisons of the solubility curves of known minerals with those from soils gave an indication of the major P compounds present.

The specific objectives of this study were: to determine the organic and inorganic P; to estimate the proportion of different forms of inorganic P; to investigate the contribution of these inorganic P fractions to the P extracted by three reagents used for estimating "available" P in soils of East Baton Rouge Parish, Louisiana, and to find the effect of the amount of clay and pH on P extracted by the soil test reagents.

REVIEW OF LITERATURE

The development of soil test methods for phosphorus (P), has been mainly concerned with chemical procedures to determine: (a) the easily-soluble portion or "available" P level in soils considered to have a specific effect in plant nutrition; (b) the organic and inorganic fractions of soil P as a total and taking in account that the total "available" P is a summation of the available organic and inorganic portions, and (c) with the application of the relatively more recent techniques to fractionate the organic and inorganic P combinations by using a selective dissolution analysis, as an approach to the understanding of soil P behavior.

Chemical procedures for determining "available" phosphorus in soils were first proposed more than a century ago. Review of the methods in regard to the origin and merits of various extractants, the effects of soil to solution ratios, and the chemistry of the soil easily-soluble, extractable or "available" P have been reported by Byrnside and Sturgis (18)[1]; Fitts and Nelson (37); Metson (67); Nelson, Mehlich and Winters (69); Peech (77); Reed and Sturgis (83); Rubins and Dean (84), and many others. The interpretation of soil phosphorus values in relation to plant response to fertilizers, still remains in some cases a difficult undertaking (18).

Methods to study the organic and/or total soil P have been suggested or observations reported by Anderson (5), Auten (6), Barrow

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[1] Numbers in parenthesis refer to Literature Cited.

(7), Bray and Kurtz (16), Caldwell and Black (20), Legg and Black (58), Bohne, Gröpler and Dittmer (14), Mehta et al. (66), Saunders and Williams (87), Van Diest and Black (100), Williams and Steinbergs (105), Williams, Williams and Scott (106), and some others. Although the Mehta et al. method (66) has been widely accepted to evaluate the total, inorganic and organic fractions, Caldwell and Black (20) pointed out that little work has been done on the best methods for extracting inositol hexaphosphates.

Studies on inorganic soil P fractionation have been presented by Al-Abba and Barber (2, 3), Bhangoo and Smith (10), Byrnside and Sturgis (18), Chang and Jackson (24), Dean (29), Fiskell and Spencer (36), Hamilton and Lessard (45), Pratt and Garber (78), Patel and Mehta (75), Saeki and Okamoto (86), Talibudeen (94), Williams (104) and others. The technique proposed by Chang and Jackson (24) has been adapted in different countries including Europe (73) and the Far East (25).

A partial fractionation as related to response of sugar cane to fertilizer P in Louisiana, was conducted in 1958 by Byrnside and Sturgis (18), and, in the prosecution of the present work, it was considered that "relatively little information is available in Louisiana on the relationships of soil phosphorus and its fractions" to specify its importance as a source of this nutrient to plant growth.

A review of concepts dealing with these points of view, is presented.

Easily soluble or "available" P.- The Olsen et al. method (70) using 0.5 molar solutions of $NaHCO_3$ at pH 8.5 is based on the increased solubility of Ca-phosphates as a result of decreasing the Ca^{++} ion

activity in solution (27). The extractant is assumed to remove about one half P on the surface of soil particles that readily exchanges with P^{32} in the soil solution, and minimuzes secondary precipitation and adsorption reactions. Olsen and Watanabe (71) also found that P adsorption by soils from dilute solutions showed a closer agreement with the Langmuir isotherm than with the Freundlich isotherm. The adsorption maximum calculated from the Langmuir isotherm was well correlated with the surface area of soils as measured by the ethylene glycol retention. They concluded that acid soils retained more P per unit of surface area and that the P is retained with a greater bonding energy than the alkaline soils.

From a comparison of the amounts of P removed from different soils by various extractants, Breland and Sierra (17) found that the efficiency in removing P followed the decreasing order: 0.025 HCl + 0.03N NH_4F, 0.05N HCl + 0.025N H_2SO_4, 0.5M $NaHCO_3$, NaAc, NH_4Ac., distilled water, 0.002N H_2SO_4, and distilled water + CO_2. They also concluded that soils high in P required a longer extraction to reach equilibrium than those low in P but no more than 10 to 15 minutes. According to Datta and Kamath (28) the performance of the $NaHCO_3$ method in Indian soils was the best and most satisfactory, with highly significant correlations, in most of the cases with wheat and rice soils.

Haddock and Linton (44) studied the relationship between $NaHCO_3$-soluble P and P in peas. They founded a significant regression for plant samples harvested 55 days after planting but not for plant samples harvested 75 days after planting. It was assumed that rate of natural soil-P supply at the 55-day period was inadequate to maintain plant-P at levels for best plant growth.

Olsen, Dreier and Rhodes (72) concluded from their studies in Nebraska, that the Bray and Kurtz (16), and $NaHCO_3$ extractions are reliable methods on calcareous soils.

Studies conducted by Pratt and Garber (78) indicated that the P-extracted by $NaHCO_3$ was positively correlated with NH_4Cl-soluble, NH_4F-soluble, and NaOH-soluble P, but the effect of increasing clay content in decreasing the effectiveness of $NaHCO_3$ reagent was related to the exhaustation of the reagent and secondary precipitation.

Swaminathan (92), in India found that the Olsen test gave the maximum degree of correlation with response of potatoes to phosphate. The contrary was observed in New York soils by Lathwell et al. (56). Thompson and Pratt (96) reported that the 0.5 molar $NaHCO_3$ solution extracted amounts of P from Ohio soils that accurately estimated plant-available P in lucerne and maize crops, but Tseng and Wang (98) in determining the "available"-P of paddy soils in Taiwan, reported that Olsen's test extracts too little available-P for accurate estimation of P needs. Williams and Cooke (108) working with grasses and potatoes state that the $NaHCO_3$ extractant was the best.

The Ammonium Acetate buffered extracting solution for P, was proposed by L. C. Kapp. Kapp investigated various ratios of ammonium acetate and HCl and came upon a procedure that apparently extracted an important fraction of P from the soil (19).

Mäkitie (63) expresses that ammonium acetate is commonly used in Finland, but that it is buffered to pH 4.65. The extract gives P values that are used for interpretation of the level of easily soluble-P in soils. It is emphasized that in spite of all the research on soil-P, relatively little attention has been paid to the origin of the P which

is extracted by a strongly buffered ammonium acetate at a more "natural" acidity, e.g., at pH 4.65. He points out that the extractability of the P of acid soils is proportional to the amounts of P adsorbed by Al and Fe.

It is well known that available soil P occurs in more than one form. Bray and Kurtz (16) observed in the Corn Belt soils that below pH 6 the adsorbed forms of P are more abundant than at higher pH values, and when soluble phosphates were added these "adsorbed" forms increased, but they remained more stable above pH 6. A lyotropic series to replace the "adsorbed" P was presented by Kurtz et al (55) with the following increasing order of anions: chloride, sulfate, thyocianate, acetate, borate, bicarbonate, citrate, oxalate, fluoride. The outstanding replacing capacity of the fluoride ion induced Bray (15, 16) to use NH_4F together with HCl in extracting soil P. Ghani and Islam (40) studying Pakistan soils found that the ratio of fluoride-soluble to oxalate-soluble P was fairly constant and on the average 1.61. Smith and Cook (90) correlated the "available" P with the response of wheat in several Michigan soils and obtained a reliable chemical measure of the "available" P when they extracted "adsorbed" P with fluoride.

According to Datta and Kamath (28), no simple form of chemical analysis can give reliable measure of availability under all conditions. Success depends to a very large extent upon careful calibration of results of chemical tests with response of crops to application of fertilizers on different soils. Bishop and Barber (11) consider that "available" P will be the P available to the plant as indicated by plant growth experiments. They concluded that "available" P is influenced

by such factors as soil pH, nature and amount of soil P compounds, clay content and type of clay minerals present. They emphasized that where several of these factors vary among soils, it is logical to assume that no one extracting solution can be expected to produce results correlating well with available P under all conditions.

The total and organic phosphorus fractions.- Bray and Kurtz (16) suggested that the organic forms of P are of importance in soil fertility because they are an indirect source of soluble forms. These soluble forms in later periods may counter balance the effect of crop removal.

In the method for organic P evaluation in soils proposed by Mehta et al. (66), the total P is measured and the inorganic P subtracted to define the amount of the total organic P fraction.

Anderson (5) has proposed a partial fractionation of the alkali-soluble soil organic P by pH adjustment. At pH 0.2 DNA was precipitated, but not inositol hexaphosphate. Precipitation increased up to pH 2.3 e.g. inositol hexaphosphate and DNA were precipitated at pH 2.9 in the presence of added aluminum.

Auten (6) studying the organic P of soils concluded that organic P, probably does not exist in appreciable amounts as nucleic acid, phytin, or lecithin; it is not an accumulation of pyrimidine nucleotides, and when added to soils it may be hydrolyzed and the inorganic P forms may combine with calcium, magnesium or other metal of an organic amphoteric complex.

Barrow (7) considers the occurrence of P in organic matter is not in any characteristic proportion. Only a small portion of organic P occurs in nucleic acids, and a variable portion as inositol phosphates-mainly the hexaphosphates.

The presence of inositol hexaphosphates have originated different points of view. For some investigators (105, 106) the variation in this constituent may account for variation in the P content of the organic matter. The opposite finding, showing that inositol hexaphosphates did not accumulate when the P content of the organic matter was high, has been demonstrated by Thomas and Lynch (95). Such facts are in accordance with Caldwell and Black (20) in the sense that little work has been done on the best methods for extracting inositol hexaphosphates.

Van Diest and Black (100) compared the methods of Mehta et al. (66) using concentrated HCl and that of Kaila and Virtanen (53) in both cases completing the extraction with 0.5N NaOH, first at room temperature and then at 90° C. The method of Mehta et al. gave higher values of organic P in different silt loams and a peat soil.

Dyer and Wrenshall (31) were of the opinion that organic P in soils is an accumulation of compounds which are resistant to further decomposition. Acid soils usually contain more organic P than calcareous soils. Liming is expected to hasten decomposition of organic P compounds and so improve the P status. Phytin may accumulate in acid soils by forming insoluble combinations with sesquioxides. In neutral and alkali soils it remains still relatively resistant.

Other organic P compounds as nucleic acids and unidentified substances can be present in soils. Traces of lipid-P have been evident.

It is evident according to Russell (85) that more work has been done on the factors controlling the liberation of phosphate by organic matter decomposition than its lockup due to humus accumulation.

It has long been recognized that significant proportions of the total soil phosphorus occur in organic combinations (32). Black and Goring (12), Dickman and DeTurk (30), and Pearson (76) have shown that the organic phosphorus fraction amounts in some cases to more than half of the total phosphorus in the surface six inches.

Shorey, Auten, and others as cited by Dean (29) have suggested that the organic P of soils are mostly nucleic acids and their derivatives. When nucleic acids are oxidized under some conditions they are converted into nucleotides and no inorganic P is liberated. The fact that organic P in mineral soils is directly related to the organic carbon or organic matter content may be taken to imply that the organic P is mainly a function of plant and biological activities.

In 1938, Dickman and DeTurk (30) described a method for the determination of the organic P which is based on the liberation of P by decomposition of the organic matter with hydrogen peroxide and subsequent extractions with 0.2N H_2SO_4. The procedure is comparatively simple and rapid, and does not have significant effect on the inorganic constituents. The difference between the P content of the extracts of the oxidized and the unoxidized soil was taken as a measure of the organic P.

In 1954, Metha et al. (66) described the well known method of successive extractions with concentrated HCl and 0.5N NaOH cold and at 90° C. The difference between the total-and inorganic-P contents of the combined extracts was taken as the total organic P.

Besides the previous methods to determine organic P the ignition method as proposed by Legg and Black (58) has been also used. Kaila (51) comments that Mehta's method of extracting organic P by successive

treatments with concentrated HCl at temperatures up to 70° C, 0.5N NaOH at room temperature, and 0.5N NaOH at 90° C. produced values similar to the simpler procedure of successive extractions of 2 g soil with 50 ml of 4 molar H_2SO_4 and 200 ml of 0.5N NaOH at room temperature. The ignition method (58) yielded values that were on the average, 50 ppm higher in surface soils and 20 ppm higher in the lower horizons than those yielded by extraction.

Studies of organic P in Finnish soils by Kaila (49, 52) indicate that in cultivated mineral top soils the P content ranged from 100 to 940 ppm, with an average figure of 340 ppm, and this was attributed to soil heterogeneity and to a large number of biological, chemical and physical factors involved.

Saunders and Williams (87) studied the validity of total organic P values. They found that results by hot-ammonia extraction are markedly dependent on the acid pretreatment, but irrespective of this, the values obtained are much lower than by the ignition method. The attributed causes were: incomplete extraction and hydrolysis of organic P, and also, 0.1N NaOH is much better than 0.5N NH_4OH as an extractant for organic P.

Observations in Ohio soils made by Schollenberger (88) indicate that soil reaction appears to be without influence upon the quantity and nature of the organic P and that the organic P compounds are decomposed slightly more readily in cultivated soils than in virgin soils.

Bohne, Gröpler and Dittmer (14) in 1958, proposed a method to determine the total soil P by means of $HClO_4$ digestion and then using the proper amounts of the reagent for determinations with the vanadate-

molybdate method. They claimed and cited that the P values obtained by this method agreed well with other techniques which consume larger amounts of $HClO_4$ and require a longer time for digestion, due to the simultaneous applications of HNO_3. Bray and Kurtz (16) for the determination of total P in soils adopted a method in which the P is determined directly in an aliquot from the original digestion, in a semi-micro way if desired, and where arsenic and iron do not interfere when present in appreciable but not excessive amounts.

Bogdanov (13) in Siberian chernozem soils found differences between the average total P contents of different subtypes of chernozems related to differences in humus content, total P increasing with increase in humus. The highest total P and humus content occurred in podzolized and leached chernozems and lowest in the southern chernozem. Such a relationship in a given subtype of chernozem was affected by variations in soil formation in the various gemorphological regions. The organic P is also related to the genetic subtype of chernozem and regional differences in the relative age of the chernozems have a more marked effect on the content of organic P than on total P.

Godfrey and Riecken (41) found in loess-derived soils along a traverse from southeastern Iowa to northern Missouri, that total P decreased in the profile along the traverse in relation to the degree of profile development. The weathering action reduced the amount of P in A horizons. In B horizons the amount of P was less than in the A or C horizons. Organic P also decreased in relation to the degree of profile development along the traverse and declined vertically in the profiles.

Shawari and Moustafa (89) studying the status of P in Egyptian soils found that the average total P content varied between 0.1323 and 0.3501 per cent in basin soils, and 0.0966 and 0.2591 per cent in irrigated soils. The maximum level of total P in basin soils occurred at 75 to 100 cm depth. There was a gradual decrease of total P from the top layer downwards in irrigated soils.

Vintila, Bajescu and Chiriac (101) report from Rumanian soils that in the surface layer, mineral P represent 50 to 70 per cent of the total. It is least abundant in brown podzolic soils forming 1 to 4 per cent of the total. The content of organic P varies from 30 to 50 per cent of the total.

Patel and Mehta (74) studying the vertical distribution of total and "available" P in soil profiles of Gujarat, India, inform that the top layer was richer than the subsoil in both total and available P.

Fractionation of soil inorganic phosphorus.- Previous works on this subject have been reported by Fraps (38) in 1906, Fisher and Thomas (35) in 1935, Williams (107) in 1937, Dean (29) in 1938, Gahni (39) in 1943, Williams (103) in 1950, and Chang and Jackson (24) in 1957.

Dean (29) in an attempt to fractionate the soil P made extractions of soils with NaOH, followed by an acid. The P compounds of the soils were divided into three fractions: (a) organic compounds soluble in NaOH; (b) inorganic compounds dissolved by extraction with NaOH followed by an acid; and (c) insoluble compounds. The solubility of inorganic phosphatic materials in NaOH revealed that tricalcium phosphate and apatite were relatively insoluble, while iron

(Fe), aluminum (Al), mono-and dicalcium phosphates were soluble. Further the presence of free calcium in solution depressed the solubility of such previous compounds.

In the other procedures followed by investigators mentioned above, iron-and aluminum-P were combined into the same fraction.

Turner and Rice (99) in 1954 found that neutral NH_4F can dissolve Al-P but not Fe-P. Then, the fraction obtained with this extractant by Bray and Kurtz (16) might be expected to be predominant in Al-P. In some of these methods (39, 103) the acid extraction which preceded the alkali extraction was shown to remove not only Ca-P but also considerable Al-and Fe-P. The P-combination insoluble in alkali and acid was shown to be reductant soluble but its nature has been only partly characterized.

With such criteria Chang and Jackson (24) classified the inorganic P compounds into four main groups: Ca-P, Al-P, Fe-P, and the reductant soluble P extractable after removal of the first three forms. Ca-P exists mainly as apatite, but dicalcium, monocalcium, and octacalcium phosphates also exist in small amounts or as transitional forms. Fe-, Al-, and Ca-P also include adsorbed and surface-precipitated P associated with the respective types of soil particles.

In a following study, Chang and Jackson (23) state that the distribution of soil inorganic P was found to measure the degree of chemical weathering, the chemical weathering sequence being Ca-P, Al-P, Fe-P and occluded P which includes reductant soluble Fe-and Al-Fe-P occluded in Fe-oxides.

Another previous study has been the procedure proposed by Aguilera and Jackson (1) in which use is made of Na-dithionate as a

reductant, and 0.3 molar Na-citrate with or without Fe-3 specific versene as the chelating reagent to remove Fe-oxide coatings or crystals from soils. The reaction is fast and does not precipitate either elemental sulphur or Fe-sulfides.

Bauwin and Tyner (8) postulated that the non-extractable-P present in soils might be occluded in the Fe-coatings of weathered colloidal silicates or in micro-concretions (9). Solutions of the total soil P was achieved only when the secondary Fe-compounds were reduced by the Deb Na acetate-Na tartrate buffered Na-hydrosulfite procedure. The P brought into solution by the buffered Deb procedure was termed "reductant-soluble" instead of "unextractable" P previously used in describing the insoluble P fraction.

Bhangoo and Smith (10) studying some virgin soils in Kansas found that Fe-and Al-P accounted for somewhat more than half of the total P in surface material, and about two-thirds in subsoils.

In the Bray and Kurtz's method (16) the neutral NH_4F was suggested as a reagent for removing the adsorbed forms of phosphate and separating them from the acid soluble forms. Then the acid soluble forms can be calculated by difference when the acid soluble forms are first dissolved in acid without NH_4F and in acid with NH_4F.

Chai and Caldwell (22) express that fractionation of the inorganic P showed that Fe-and Al-P were abundant in acid soils while Ca-P was abundant in alkaline soils and that in soils having a pH near 7.0 all three forms of inorganic P were about equally distributed, though slightly more Fe and Al than Ca-P were present. In the same sequence of ideas, Chu and Chang (26), studying the soils of Taiwan indicate that three different distribution patterns occur: Ca-P, Al-P, and Fe-P.

The Fe-P dominant in latosols, the Ca-P present in calcareous alluvial soils, and the Ca and Fe-P forms dominant in acid, sandstone and shale alluvial soils.

Fife (33, 34) expresses that P-compound solubility in systems containing $Fe(OH_3)$ was shown to reach a minimum value in the vicinity of the neutral point, and in view of the almost universal occurrence of free Fe-oxides in soils it was concluded that satisfactory delineation of Al-bound soil P is unlikely to be attained by the use of 0.5 molar NH_4F at pH 7.0. It was suggested the use of a fluoride solution sufficiently alkaline to inhibit resorption of P-forms by free Fe-oxides. The results obtained were consistent with Fe-bound soil P resistant to alkaline hydrolysis in 0.5 molar NH_4F and showed that the most general selective delineation of Al-bound soil P is attained at pH 8.5.

Chang and Liaw (25) studying the separation of Al-P from Fe-P in soils found Al-P forms to be more discretely separated from Fe-P by extracting 1 g. of soil with 50 ml. neutral 0.5 molar NH_4F solution for one hour, than by extracting with alkaline solution for a longer period.

Turner and Rice (99) studying the role of fluoride ion in the release of P adsorbed by Al and Fe-hydroxides particularize that neutral NH_4F reacts with $Al(OH_3)$ gels to form $(NH_4)_3\ AlF_6$ and the P adsorbed on these gels is released by the actions of the fluoride ion. On the other hand they say, $Fe(OH)_3$ gels are apparently not attacked by the fluoride ion. The efficiency of neutral NH_4F as an extractant of phosphate adsorbed by $Al(OH)_3$ is explained by the stability of the trivalent fluoraluminate complex ion in neutral and alkaline solution, the P adsorbed being made soluble by the direct action of the fluoride ion on the gel with the

formation of a non-adsorbent Al-fluoride complex. Apparently the trivalent fluoro-ferrate ion, formed in acid solutions is destroyed in neutral and alkaline solutions with the formation of $Fe(OH)_3$.

Lindsay, Peech and Clark (59) indicate that since the Ca-P forms are too soluble to persist in soils below pH 6.0, it has been assumed that the Al-and Fe-P and less soluble forms (variscite and strengite) may be the ultimate end products of phosphate fixation in acid soils.

Rathje (82) showed experimentally that synthetic soil-P minerals (hydroxyfluorapatite, Al-and ferric hydroxide-phosphate) exist in the following equilibrium with one another.

$$\text{Ca-phosphate} + \left.\begin{matrix}\text{Al}\\ \text{Fe}\end{matrix}\right\}\text{hydroxide} = \left.\begin{matrix}\text{Al}\\ \text{Fe}\end{matrix}\right\}\text{"hydroxide phosphate"} + \text{CaOH}.$$

Equilibrium is shifted to the left by an alkaline reaction and to the right by an acid reaction, and according to Swenson, Cole and Sieling (93) the mechanism of phosphate fixation by Fe and Al can be represented by the following equilibrium reaction:

$$Al(H_2O)_3 \begin{matrix}OH\\ OH\\ OH\end{matrix} + H_2PO_4^- = Al(H_2O)_3 \begin{matrix}OH\\ OH\\ H_2PO_4\end{matrix} + OH^-$$

Laverty and McLean (57) applying the Chang and Jackson phosphate fractionation procedure found that soils of low fixation tied up 2.5 times as much P in the Al-P fraction as in the Fe-P fraction, while the reverse was true with soils of high fixation. This suggests that the Al-P fraction is considerably more available to plants than is the Fe-P fraction. Middleton (68) reports from Sudan, that lateritic soils have a low content of total and available P.

Kaila (50) reports that podzolized virgin soils are low in all forms of inorganic P in the upper layers, especially in the A_2 horizon. At depths below 30-40 cm, the P is bound to Ca in all soils but in cultivated soil alkali soluble P bound to Fe predominates at all depths. Jahn-Deesbach (48) gives figures on the P content in profiles of several chernozems from Germany, Czechoslovakia and the Ukrania. More than 50 per cent is Ca-P and the rest is in combination with sesquioxides. Inorganic and organic P decrease with soil depth.

Weir and Soper (102) observed in Manitoba soils that adsorption of P closely followed the Langmuir isotherm at solution concentrations lower than 25 to 30 ug. P/ml. The amounts of adsorbed P equilibrated with P^{32} decreased with increasing $CaCO_3$ percentage. Similar conclusions were given by Cole and Olsen (27).

Soil Phosphorus Relationship with pH, N and Texture.- In a study of regression analysis of the P fractions with available P, Al-Abbas and Barber (2) used soil pH and organic matter as inedpendent variables since both influence P availability.

Pratt and Garber (78) studied the effect of texture and pH on the P availability extracted by three reagents: water, Bray, and $NaHCO_3$. The ineffectiveness of the Bray reagent for clayey soils (> 20 per cent clay) was attributed to a secondary reaction after dissolution and/or as a result from exhaustation of the reagent by reaction with soil minerals, other than phosphates.

Caldwell and Black (20) found that the percentage of inositol hexaphosphosphate in relation to total organic P was higher in forest soils than in grassland soils and decreased with increasing pH.

Hsu and Jackson (46) studied the solubility of (a) hydroxy-apatite (Ca-P), (b) variscite (Al-P), and (c) strengite (Fe-P) and plotted them as a function of pH on the basis of their solubility. The solubilities of (b) and (c) were close to each other and about equal to (a) at pH 6.0 to 7.0. Above this pH (a) was more stable than (b) and (c), and below this pH (b) and (c) were more stable than (a). The inorganic P fractions in gray brown podzolic soils derived from calcareous parent materials were closely related to soil pH.

Alinari et al. (4) extracted soils with solutions varying in pH and their results indicated that P solubility was higher at pH 5.5 to 6.5 in productive than in less fertile soils, and was fairly high at pH 3.5 to 4.5 with calcareous soils.

In Finland, Kaila (49) learned that in the clay soils and in the humic soils the content of organic P was associated with the content of acid-oxalate soluble Al, but in the sandy soils no positive correlation was observed between organic P and the factors which may be responsible for stabilization of such organic P compounds as phytates.

In east Pakistan soils, Karim and Khan (54), found that the percentage of total P represented by organic P increased from pH 4.2 to pH 4.6; decreased to a minimum between pH 4.6 to 5.6 and they increased again with pH. The sesquioxide-bound P content increased with increasing pH up to pH 5.6 and then decreased as the pH increased from 5.6 to 6.2. The content of the adsorbed P increased with increasing pH between pH 4 and 5.3 and then decreased. They concluded that critical effects of pH 5.6 and 5.3 may be due to changes in the state of Fe and Al with changing pH.

MacLean, Doyle and Hamlyn (62) reported that in soils from New Brunswick Bray's values of "adsorbed" P and adsorbed + acid-soluble P were negatively correlated with the clay content of soils.

Mackenzie (61) making reference to Ontario soils indicated that isotopic exchange studies showed in most of the soils Al-P was in equilibrium with the water soluble P and that exceptions were a result of high or low pH values.

Markovskiĭ and Ponomareva (64) made a separation of soil particles in two groups: finer than 0.01 mm and coarser particles. The coarse particles adsorbed practically no $H_2PO_4^-$ from added KH_2PO_4, and the other group absorbed more orthophosphate per unit weight. The adsorption of P from various soil types and even from different samples of the same type varied considerably.

Goldsztaub, Hénin and Wey (43) showed that maximum adsorption of phosphate by Na-and Ca-montmorillonite and kaolinite occurs at pH 4 to 5.0 and agrees with the calculated value for edge-adsorption.

Martínez de Pancorbo and Lucena Conde (65) found in soils of Spain a very significant correlation between soil pH and the ratio of available to total P for different methods used. For soils with pH's higher than 7.0 there was a positive correlation for all extractants except CO_2 and $NaHCO_3$, for which correlation was negative or absent.

Pratt and Garber (78) found that the higher the clay content, other factors being equal, the lower the $NaHCO_3$-extractable P. In both the Bray-extractable P and the $NaHCO_3$-extractable P an increase in clay content appears to decrease the efficiency of extraction of P.

Pratt, Halowaychuk and Morse (79) studied the level of soluble P in Ohio soils at the 0-6 inch and 6-12 inch horizons of a wide range

of soils by extraction with 0.3N NH_4F in 0.025N HCl (P_1) or with 0.03N NH_4F in 0.1N HCl (P_2). The soluble P generally decreased with increasing depth and rarely exceeded 2.5 ppm P in horizons below 20 inches. The ratio of P_2 and P_1 could be used as an index of the relative amounts of acid soluble P.

Pratt and Shoemaker (80) from studies on acid and alkali soluble P in relation to soil reaction found through measurement of acid and alkali-soluble P after incubation, that liming did not alter the system from one in which alkali-soluble P predominate to one in which acid-soluble P predominated.

Rangland and Seay (81) studying the effects of exchangeable Ca on the retention and fixation of P by clay fractions in Kentucky soils, found that initially Al-saturated clay retained much more of added P but fixed no more of it than the initially acid saturated clay. P fixation by clay with "natural" base saturation decreased with increasing pH, whereas fixation by initially acid saturated clay increased or remained unchanged with increasing pH. Temperature and moisture also affect the P behavior (60).

Saeki and Okamoto (86) studied P fractionation from phosphated ARIMA-bentonite and SETA-kaolinite by Jackson's procedure and showed under acid conditions that Al and Fe were most effective for P fixation. In alkaline conditions the proportion of R_2O_3-P in total fixed P was less pronounced and the ratio of Ca-P was also low. P fixation was always greater in the presence of Ca^{++} than in the presence of Na^{+} ions, presumably because Ca^{++} activated more Al^{+++} ions.

Schollenberger (88) indicates that the reaction of the soil appears to be without influence upon the quantity and nature of the organic P

present. However, Stelly and Pierre (91) related pH with different forms of inorganic P in the C horizons of some Iowa soils and they concluded that apatite and rock phosphate had similar P solubility curves. The curves for the two Al-minerals (variscite and wavelite), showed a minimum solubility between pH 4.5 to 6.5. The P in wavelite was somewhat more soluble than in variscite. Dufrenxite was found to have a maximum solubility range between pH 3.0 and 6.0 and considerable lower solubility at all pH values than the Al-phosphate minerals. Vivianite showed a narrow range and minimum P solubility at pH 6.0 to 6.5.

Swenson, Cole and Sieling (93) concluded that maximum precipitation of basic Fe-P was between pH 2.5 to 3.5 whereas for basic Al-P it was from pH 3.5 to 4.0. This is the range at which $H_2PO_4^-$ predominates. This also indicates that the $H_2PO_4^-$ is the phosphate ion which reacts to form chemically combined phosphate. In relation with P availability Carbonell (21) has also made the same conclusions.

In Kampur soils from the Indian Gangetic alluvium, Goel and Agarwal (42) found that the P contents decreased with the maturity of soils. In general, higher P concentrations were found in the clay fractions, but for the whole soil, maximum P concentration occurred in the finer fractions in immature and submature soils and in the coarser fractions in mature soils. It is assumed that immature soils having most of their P in the clay fraction are better suppliers of P to crops.

Yuan (109) studying the newly fixed P in acid sandy soils, made successive extractions with 1N NH_4Cl, 0.5N NH_4F, 0.1N NaOH and 0.5N H_2SO_4 solutions to represent water soluble Al-, Fe-, Ca-P respectively. Over 80 per cent of the added P was retained by the soils as Al-and Fe-P. Less than 10 per cent was in the water soluble and Ca-P forms.

MATERIALS AND METHODS

Soil Samples.- Forty-seven soil samples were obtained from fifteen locations in East Baton Rouge Parish. The soils in this area are included in the Loessial Terrace Soils of Louisiana. Morphological differentiation in these soils is evident due to a variable degree in soil development. From each location topsoil and subsoil samples, pertaining to fifteen representative profiles, were chemically analyzed. Topsoil samples included soil profile horizons as to give a minimum depth of 6 inches. In most of the cases the two upper soil horizons satisfied this requirement. The tendency has been to evaluate the soil P pertaining to the plowed layer. The corresponding subsoil samples were obtained in each case from a non specific depth, but taking in account the most representative subsoil-horizon. Most of the topsoil samples contain less than 20 per cent clay. All the subsoils contain more than 20 per cent clay. The pH values in the topsoil samples ranged from 4.8 to 7.4 with predominance to the acid side of this range. In subsoils the pH variation was from 5.0 to 8.2 but only four samples were moderately alkaline. The per cent of total nitrogen (N) was always higher in the upper horizon where it ranged from 0.043 to 0.331 per cent but the average value for topsoils was 0.0906 per cent. In the subsoils the percentage of N varied from 0.007 to 0.066 per cent and the average figure was 0.0402 per cent.

Identification of the soils, their slope, natural drainage, classification and location are indicated in Table I. A more complete description will be available with the publication of the soil survey of East Baton Rouge Parish.

Table I.--Site number, series, subgroup, parent material, slope, drainage class, and location of soil samples.

Site No.	Series	Texture	Subgroup[1/]	Parent Material	Slope	Drainage Class	Location
3	Bonn	sil	Typic Natraqualf	Loessial terrace	0-1%	Poorly drained	A. L. Forbes
16	Olivier	sil	Aquic Fragiudalf	Loessial terrace	0-1%	Somewhat poorly drained	Perkins Rd. Farm
20	Fred	sil	Aquic Normudalf	Loessial terrace	0-2%	Moderately well drained	Essen Lane - 1
32	Deerford	sil	Udalfic Natraqualf	Loessial terrace	0-1%	Moderately well drained	Essen Lane
41	Fred	sil	Aquic Normudalf	Loessial terrace	0-2%	Moderately well drained	Essen Lane - 2
42	Lafe	sil	Aeric Natraqualf	Loessial terrace	0-1% depressed	Poorly drained	Perkins Rd. Farm
43	Foley	sil	Ochraqualfic Natrudalf	Loessial terrace	0-1%	Imperfectly drained	Perkins Rd. Farm
44	Deerford	sil	Udalfic Natraqualf	Loessial terrace	0-1%	Moderately well drained	Zachary
45	Frost	sil	Typic Glossaqualf	Loessial terrace	0-1% depressed	Poorly drained	Duke Farm
46	Deerford	sil	Udalfic Natraqualf	Loessial terrace	0-1%	Moderately well drained	Doughorty Farm
48	Loring	sil	Typic Fragiudalf	Loessial hill	1-3%	Moderately well drained	Quail Farm
52	Cahaba	sl	Typic Normudalf	Sandy terraces	1-3%	Well drained	Millican Farm
54	Memphis	sil	Typic Normudalf	Loessial hill	0-2%	Well drained	Rose Garden
58	Memphis	sil	Typic Normudalf	Loessial hill	1-2%	Well drained	Townsend Farm
63	Fred	sil	Aquic Normudalf	Loessial terrace	0-1%	Moderately well drained	Judge Farm

1/ According to the 7th Approximation, 1960.

Methods of Analysis

Easily Soluble Phosphorus Analysis.- Three different soil test procedures were used so that their results could be correlated with the results of the inorganic soil phosphorus fractionation and with other determinations included in this study. These procedures were as follows:

The Olsen Test (70).- This test consisted of shaking 5 g. of soil with 100 ml. of 0.5 molar $NaHCO_3$ adjusted to a pH 8.5 with NaOH, and addition of one teaspoon of activated carbon, for 30 minutes. The solution was filtered off and its P content colorimetrically determined in an aliquot using the molybdenum blue reaction (47).

The Ammonium Acetate Test (19).- This test consisted of shaking 5 g. of soil with the Texas Buffered Extracting solution (110 g. $NH_4C_2H_3O_2$ with 82 ml. HCl in water), adjusted to a pH 4.2, for 30 minutes; removal of the filtrate by filtration and determination of its P content colorimetrically as above.

The Bray No. 2 Test (16).- This test consisted of shaking 2.5 g. of soil with 50 ml. of a 0.10N HCl with 0.03N NH_4F for 15 minutes, filtration and colorimetric determination of the P content in the extract. Boric acid was used to counteract fluoride.

The Organic Phosphorus Evaluation

The method used was proposed by Mehta et al. (66). This method was developed with the objective of maximizing organic P extraction and to minimize hydrolysis. The content of organic P in the soil was calculated from the difference in content in inorganic and total P in the extract. The fractionation procedure was as follows:

Extraction.- One g. of soil in a 100 ml. centrifuge tube was treated with 10 ml. conc. HCl and heated to 70° C. Another 10 ml. of HCl were added immediately upon reaching 70° C. and allowed to stand at room temperature for 1 hour. After centrifuging, the supernatant liquid was poured into a 250 ml. volumetric flask containing 100 ml. H_2O. The soil was washed with 25 ml. of 0.1N HCl, then centrifuged and the liquid phase was poured into the same flask. Twenty-five ml. of 0.5 NaOH are added, stirred and allowed to stand at room temperature for 1 hour. After centrifuging the liquid is added into the same flask. The tube with the soil and 75 ml. of 0.5 NaOH was put in the oven at 90° C. for 8 hours, centrifuged and the liquid added to the flask and the volume was completed to the mark after cooling.

Determination of Total Phosphorus.- To a 15 ml. aliquot in a beaker 1 ml. $HClO_4$ was added. The excess liquid was evaporated on a hot plate until the fumes of $HClO_4$ appeared. The beaker was covered and heating continued until the organic matter was destroyed and the solution was clear. After digestion the precipitated salts were dissolved and the determination of P content made colorimetrically.

Determination of Inorganic Phosphorus.- A 20 ml. aliquot was taken from the clear liquid from the original extract and the P concentration determined colorimetrically as described above.

The difference between the inorganic P found after and the inorganic P found before the $HClO_4$ treatment was taken as a measure of the organic P in the extract.

$HClO_4$ Method for Total P (47).- A 5 g. sample of soil was transferred to a 300 ml. conical flask. In samples high in organic matter, 20 ml. of HNO_3 were added to effect preliminary oxidation on a steam

plate. Then 30 ml. of 62 per cent $HClO_4$ were added and the digestion carried out at 100 to 130° C. on a hot plate. Short tailed funnels have been used to reflux the $HClO_4$ during the digestion in the flasks. The $HClO_4$ digestion was carried out until solution appeared colorless. When the solution was cooled, 50 ml. of distilled water were added and then transferred through a filter to a 250 ml. volumetric flask. The residue was washed to bring the volume of solution to the mark.

A 50 ml. aliquot of the extract was transferred to a 100 ml. volumetric flask. P was determined colorimetrically using the vanado-molybdate procedure. The readings were made in a Bausch and Laumb photocolorimeter using a wave length of 470 mμ.

Inorganic Phosphorus Fractionation

Principle of the Method.- Before applying the method to the soils, Chang and Jackson (24) developed some control tests with Fe-and Al-phosphate (strengite variscite) synthetically prepared by using $FeCl_3$, $AlCl_3$, and NaH_2PO_4, and apatite of well-known composition. Then, the method was applied to soils of different nature. The different P-forms are extracted by different reagents:

(A) Neutral NH_4F - The fluoride ion has the property of complexing Al^{+++} and Fe^{+++} ions in acid solution liberating the bounded-P forms by these trivalent ions:

$$3\ NH_4F + 3\ HF + AlPO_4 \longrightarrow H_3PO_4 + (NH_4)_3AlF_6$$

$$3\ NH_4F + 3\ HF + FePO_4 \longrightarrow H_3PO_4 + (NH_4)_3FeF_6$$

The Fe-and Al-P are the hydrated and hydroxyl phosphates including adsorbed or precipitated surface layers on aluminosilicates or oxides. The reaction is not produced when the phosphates are covered by a film of Fe-oxide molecules (occluded phosphates).

On the other hand, in neutral or alkaline solutions, the fluoroferrate is unstable and only the Al-phosphate is extracted.

The analyses carried out on synthetic-phosphates have shown that for a P-content lower than 1 mg. in 50 ml. of 0.5N NH_4F, the Al-P solubility was complete.

The solubility of the Fe-P is small (2 per cent per 3000 ppm P and increased to 7 per cent per 100 ppm P), a correction is possible based on the Fe-P content extracted by the NaOH.

(B) 0.1N NaOH - Fifty ml. of 0.1N NaOH completely dissolve synthetic Fe-and Al-P compounds until an amount of 4 mg. P, then after extraction of the Al-phosphate by the NH_4F, the Fe-P is all extracted by the NaOH. The analysis of apatite has shown the NaOH practically does not dissolve this P-form.

(C) 0.5N H_2SO_4 - This reagent dissolves all the apatite (until a concentration of 3000 ppm P), and dissolves less than a half of the Fe-and Al-P present.

After eliminating the Fe-and Al-P forms, the H_2SO_4 extracts all of the Ca-P.

(D) The reagent Na-citrate, followed the reduction with hydrosulfite. This reagent dissolved all the synthetic Fe-P and none of the Al-P.

Analytical Procedures.- Inorganic P fractions (24) were determined as follows:

The Al-P was extracted in first place by the 0.5N and neutral NH_4F after removing water soluble and loosely bound P and exchangeable Ca with NH_4Cl. Then, the Fe-P was extracted from the residue by

the 0.1N NaOH (the Fe-P was determined after elimination of the organic-P by flocculation). After these P-forms were removed, the Ca-phosphate was extracted in the next step by means of the 0.5N H_2SO_4.

After these different extractions, there still remained in the soil an important fraction of insoluble-P, which sometimes attains as much as 40 per cent of the total P. It has been demonstrated that this fraction can be almost completely extracted by a reduction process and chelation (reagent D), this process being essentially specific of the Fe-oxide extractions. The solubilized-P was attributed to the occluded-forms in the concretioned oxides, protected by coatings of Fe-oxide that covered aggregates and concretions that were resistant to the NaOH and NH_4F, whereas the Fe-and Al-P recently precipitated or complexed with humus was largely extracted by the NaOH. The occluded-P forms are almost insoluble and so unavailable for plants.

After extractions of occluded Fe-P, by the action of Na-citrate and hydrosulfite, the occluded Al-P was extracted by NH_4F, and a residue of both Fe-and Al-P (barrandite-like) can be extracted by the NaOH.

In soil analysis this method showed a good reproductibility of results, the sum of such forms being equal to the total-P determined by fusion.

Other determinations included in this study were the Ph measured at 1:1 dilution with H_2O; per cent of clay, measured by a hydrometer method, and per cent of nitrogen (N) measured by the well-known Kjeldahl's method.

RESULTS

Total and Organic Phosphorus

Data on total, inorganic and organic P, and total N are presented in Table II. These included the depth in inches at which the samples were obtained in each of the 15 soil profiles. Total P varied as follows:

In upper soil horizons from --91 to 975 ppm of P.

Average for all surface soils --287 ppm of P.

In subsoil horizons from --73 to 375 ppm of P.

Average for all subsoils --181 ppm of P.

The content of organic P in the soil was assessed as the difference in content of inorganic and total P in the extract.

The organic P fraction was found to range as follows:

In upper soil horizons from --12 to 836 ppm of P.

Average for all surface soils --159 ppm of P.

In subsoil horizons from --1 to 117 ppm of P.

Average for all subsoils --37.5 ppm of P.

On the average 54.2 per cent of the P in surface samples was originally combined. The average in subsoil samples was 20.7 per cent in organic combination. The extreme variation for surface or topsoil samples was 7.2 per cent to 86.8 per cent and for subsoil samples practically zero to 40.1 per cent.

These results showed that organic P constituted an appreciable portion of the total P in these soils. It was observed that all subsoil samples contained less organic P than their respective surface samples.

In soils low in total P, the organic P fractions tend to amount to a relatively higher percentage of the P. The ratio of P in organic

Table III.--Total, inorganic and organic P fractions, and percentage of nitrogen in topsoil horizons and subsoil.

Sample No.	Soil depth (inches)	Total P (ppm)	Inorganic P (ppm)	Organic P (ppm)	Nitrogen %
3-1	0-1	917	79	836	0.254
3-2	1-3	198	32	166	0.041
3-3	3-8	273	69	204	0.036
3-6	16-36	103	102	1	0.007
16-1	0-5	467	256	211	0.059
16-2	5-7	432	199	233	0.040
16-5	17-22	195	125	70	0.043
20-1	0-5	375	102	272	0.056
20-2	5-7	463	86	377	0.051
20-4	13-18	292	175	117	0.046
32-1	0-1	975	234	741	0.331
32-2	1-3	558	194	364	0.265
32-3	3-8	433	81	352	0.059
32-4	8-14	133	75	58	0.066
41-1	0-6	196	128	68	0.069
41-2	6-9	196	144	52	0.059
41-4	10-18	147	76	71	0.048
42-1	0-6	208	191	17	0.077
42-2	6-10	205	193	12	0.070
42-4	20-45	237	236	1	0.019
43-1	0-3	177	107	70	0.077
43-2	3-6	168	109	59	0.064
43-4	14-28	104	60	44	0.030
44-1	0-3	177	70	107	0.050
44-2	3-6	167	88	79	0.048
44-4	10-20	73	53	20	0.064
45-1	0-3	192	85	107	0.134
45-2	3-11	91	41	50	0.042
45-4	20-32	103	51	52	0.036
46-1	0-2	205	111	94	0.120
46-2	2-11	157	60	97	0.058
46-3	11-17	133	115	18	0.031

Table II.--Total, inorganic and organic P fractions, and percentage of nitrogen in topsoil horizons and subsoil - (continued).

Sample No.	Soil depth (inches)	Total P (ppm)	Inorganic P (ppm)	Organic P (ppm)	Nitrogen %
48-1	0-4	232	109	123	0.081
48-2	4-6	247	125	122	0.080
48-4	11-22	300	288	12	0.046
52-1	0-4	212	165	47	0.043
52-2	4-10	158	133	25	0.024
52-4	13-19	168	163	5	0.029
54-1	0-4	667	159	159	0.137
54-2	4-8	653	519	134	0.091
54-4	18-36	375	322	53	0.049
58-1	0-7	217	133	84	0.090
58-2	7-11	256	163	93	0.057
58-3	11-20	243	219	24	0.047
63-1	0-3	290	168	122	0.156
63-2	3-9	150	88	62	0.082
63-4	18-23	133	115	18	0.031

form to total N, in some cases, was apparently higher in subsoil samples. On the basis of the average content of organic P and total N, the ratios were:

For surface soils Organic P/Total N = 159/910 = 0.1747

For subsoils Organic P/Total N = 37.5/420 = 0.0893

Although organic P was positively correlated (r .755) with total N, some soils higher in total N showed a lower percentage of organic P than soils lower in total N.

Easily Soluble Phosphorus and Inorganic Phosphorus Fractions.-

Data on "available" P by chemical tests, inorganic P fractions, pH, and clay content of the soils studied, are presented in Table III.

Easily Soluble or "available" P.- The extraction methods applied included a basic solution of ($NaHCO_3$) and two acid solutions (Ammonium acetate, pH 4.2 and Bray No. 2) as extractants.

In this study the total available soil P was considered as a summation of the "available" inorganic and organic P.

In using the $NaHCO_3$ solution as an extractant, it was assumed that the HCO_3^- ion reduces the activity of the Ca^{++} cation in calcareous soils and thereby increases the solubility of P (70).

The acidic extraction solutions were proposed (22) because the assumption that plant roots excrete acids and these may act as solvents. The NH_4F solution was proposed as an extracting agent because the F^- ion seemed to replace adsorbed P, and a similar performance is attributed to the acetate ion.

From the three methods used to determine P- "availability" that of Bray gave relatively higher values followed by the $NaHCO_3$ extraction, and the Ammonium acetate procedure yielded the lower figures.

Table III.--Phosphorus availability by chemical tests, inorganic P fractions, pH and clay content. All P data are in ppm. in the dry soil.

Soil No.	Availability tests			Inorganic fractions extracted by					pH	Clay
							Occluded P			
	$NaHCO_3$	Am. Acetate	Bray	NH_4F	NaOH	H_2SO_4	Na-Citrate	NH_4F		
	Y_1	Y_2	Y_3	X_1	X_2	X_3	X_4	X_5	X_6	X_7
	ppm									
3-1	7	2	17	27	25	10	15	2	5.0	9.2
3-2	2	2	3	10	12	2	5	2	5.2	9.2
3-3	2	1	5	10	12	13	30	4	4.1	11.5
3-6	3	1	54	4	8	30	55	4	7.6	22.8
16-1	20	6	60	42	126	35	45	4	5.0	6.0
16-2	12	4	35	20	105	25	45	4	5.1	5.5
16-5	5	1	5	9	45	11	45	14	5.0	29.8
20-1	6	2	9	7	50	13	30	2	6.4	19.5
20-2	5	1	7	5	40	6	25	2	6.4	21.2
20-4	2	1	2	9	32	54	65	13	6.7	31.2
32-1	16	8	34	42	126	31	30	2	5.5	13.5
32-2	11	3	30	25	100	28	30	5	5.3	13.0
32-3	4	1	4	15	24	6	30	5	5.1	17.8
32-4	3	1	3	7	20	9	25	9	5.6	30.6
41-1	7	2	13	10	50	25	35	4	6.7	17.5
41-2	10	2	13	7	80	25	25	4	6.7	17.0
41-4	3	1	2	7	20	8	30	9	7.2	29.0
42-1	18	10	55	20	75	44	50	2	7.2	20.5
42-2	17	10	51	25	90	33	30	2	7.4	19.0
42-4	11	3	40	20	50	76	80	10	8.2	28.8
43-1	12	4	30	10	38	28	25	4	6.2	18.2
43-2	7	4	22	7	33	35	25	4	7.0	18.8
43-4	4	1	7	4	10	16	20	9	8.0	29.0

Table III.--Phosphorus availability by chemical tests, inorganic P fractions, pH and clay content. All P data are in ppm. in the dry soil.- (continued).

Soil No.	Availability tests			Inorganic fractions extracted by					pH	Clay
							Occluded P			
	$NaHCO_3$	Am. Acetate	Bray	NH_4F	NaOH	H_2SO_4	Na-Citrate	NH_4F		
	Y_1	Y_2	Y_3	X_1	X_2	X_3	X_4	X_5	X_6	X_7
	ppm									
44-1	6	1	10	4	38	9	15	4	5.9	8.8
44-2	6	1	8	7	40	13	20	5	5.9	8.5
44-4	2	1	5	4	10	2	30	4	5.3	31.8
45-1	11	4	18	17	21	8	30	4	5.4	13.8
45-2	4	3	5	5	7	18	5	4	5.4	13.6
45-4	2	1	4	7	12	9	15	4	5.1	33.5
46-1	6	2	8	10	30	10	45	14	5.7	13.0
46-2	3	2	5	2	15	6	30	4	5.9	18.0
46-3	2	2	3	9	10	5	15	9	6.2	31.8
48-1	6	3	10	5	28	15	50	4	6.5	12.0
48-2	4	1	7	5	21	10	40	2	6.0	14.8
48-4	6	1	9	20	100	46	100	14	5.2	29.0
52-1	55	17	98	70	30	5	40	2	5.0	4.0
52-2	38	17	75	55	26	8	40	4	4.8	6.0
52-4	5	1	5	12	40	25	70	12	5.1	27.0
54-1	67	22	265	132	194	68	100	4	6.5	9.0
54-2	98	29	274	132	206	63	100	14	6.3	11.0
54-4	32	4	64	20	100	88	100	12	5.3	27.5
58-1	5	1	6	5	28	16	75	9	6.0	18.2
58-2	4	1	2	5	26	15	100	15	6.0	29.2
58-3	6	1	4	9	62	40	90	15	6.0	32.5
63-1	13	6	24	15	43	25	50	7	6.6	8.5
63-2	7	2	9	4	20	10	50	4	7.0	11.5
63-4	5	1	3	10	25	14	55	10	7.3	26.8

Such determinations are considered as the Y's set of variables in the correlation analysis, as shown in Table IV.

The nature of the P obtained by these quick methods was related to the inorganic soil-P fractions.

The Inorganic Soil-P Fractions.- As indicated in Table III the inorganic P fractions were extracted with different reagents. The NH_4F extraction was presumed to remove the Aluminum-phosphate form, simply expressed as Al-P because in the chemical analysis the phosphorus (P) was determined at such, NaOH the Fe-P compounds, H_2SO_4 the Ca-P forms, Na-citrate and dithionite the occluded Fe-P and a second extraction with NH_4F the occluded Al-P, all of them reported in ppm of P.

From data in Table III it is observed that the Fe-P combination extracted by the NaOH solution is the most abundant P-form in these soils. In some surface soils the Al-P form is higher than Ca-P compounds but in subsoils the Ca-P form predominate. Of the occluded-P forms the Fe-P combination is more abundant than the Al-P.

Simple and Multiple Correlation Analysis

Statistical correlations were calculated between organic P and total P, total N, and pH. The data pertaining to these items appears in Table II and the pH in Table III.

Statistical correlations of organic P with total P ($r = 0.858$) and with total N ($r = 0.755$) were highly significant as would be expected. Correlation of organic P with pH ($r = 0.306$) was just short of significance at the 5 per cent level, and it was assumed to occur because most of the soils were acid in reaction. In fact, 17 surface and 9 subsoil samples were below pH 6.5 and only 2 surface and 5 subsoil samples from a total of 47, were above pH 7.0.

Table IV.--Linear correlation coefficients for relationships among the columns and combinations of columns of data presented in Table 3.

	Y_2	Y_3	X_1	X_2	X_3	X_4	X_5	X_6	X_7
			Inorganic P extracted by						
			NH_4F	NaOH	H_2SO_4	Na-Citr.	[1/] NH_4F [2/]	pH	Clay
Y_1 ($NaHCO_3$-soluble P)	0.957**	0.949**	0.947**	0.723**	0.477**	0.441**	0.048	-0.052	-0.384**
Y_2 (Amm. Acet.-soluble P)		0.920**	0.935**	0.669**	0.386**	0.324*	-0.080	-0.017	-0.438**
Y_3 (Bray soluble-P)			0.956**	0.768**	0.545**	0.463**	0.011	0.060	-0.341*
X_1				0.767**	0.449**	0.413**	0.010	-0.103	-0.395**
X_2					0.679**	0.511**	0.106	-0.025	-0.258
X_3						0.690**	0.336	0.284*	0.131
X_4							0.642**	0.117	0.215
X_5								0.039	0.555**
X_6									0.268

** Statistically significant at 0.01 probability level.

* Statistically significant at 0.05 probability level.

1/ and 2/ Occluded P.

Figure 1 shows the linear regression equation and simple correlation coefficient obtained from the relation between organic P and total P reported in Table II.

The linear correlation coefficients for relationships among columns and combinations of columns of data presented in Table III are reported in Table IV.

From Table IV it is observed the $NaHCO_3$ extractable P was positively correlated with NH_4F-soluble, NaOH-soluble, H_2SO_4-soluble, and Na-acetate citrate soluble P, and negatively with pH and clay content.

The Ammonium acetate and Bray extractable P followed the same pattern but the occluded Al-P, pH, and clay content correlated negatively with the former and the clay content at the 5.0 per cent level with the latter.

The degree of association between variables decreased in the same order of extractions as indicated by the sequence of the P-fractions.

In the same Table IV occluded Al-P and pH columns showed a loose association between these variables except in the simple correlations between occluded Fe-P with occluded Al-P, H_2SO_4-soluble P with pH, and occluded Al-P with clay, which correlation coefficients were highly significant. The simple correlation analysis between the Y variables gave very high correlation coefficients.

A multiple correlation analysis with all the X variables included in Table III, and when certain factors were dropped, developed the following equations:

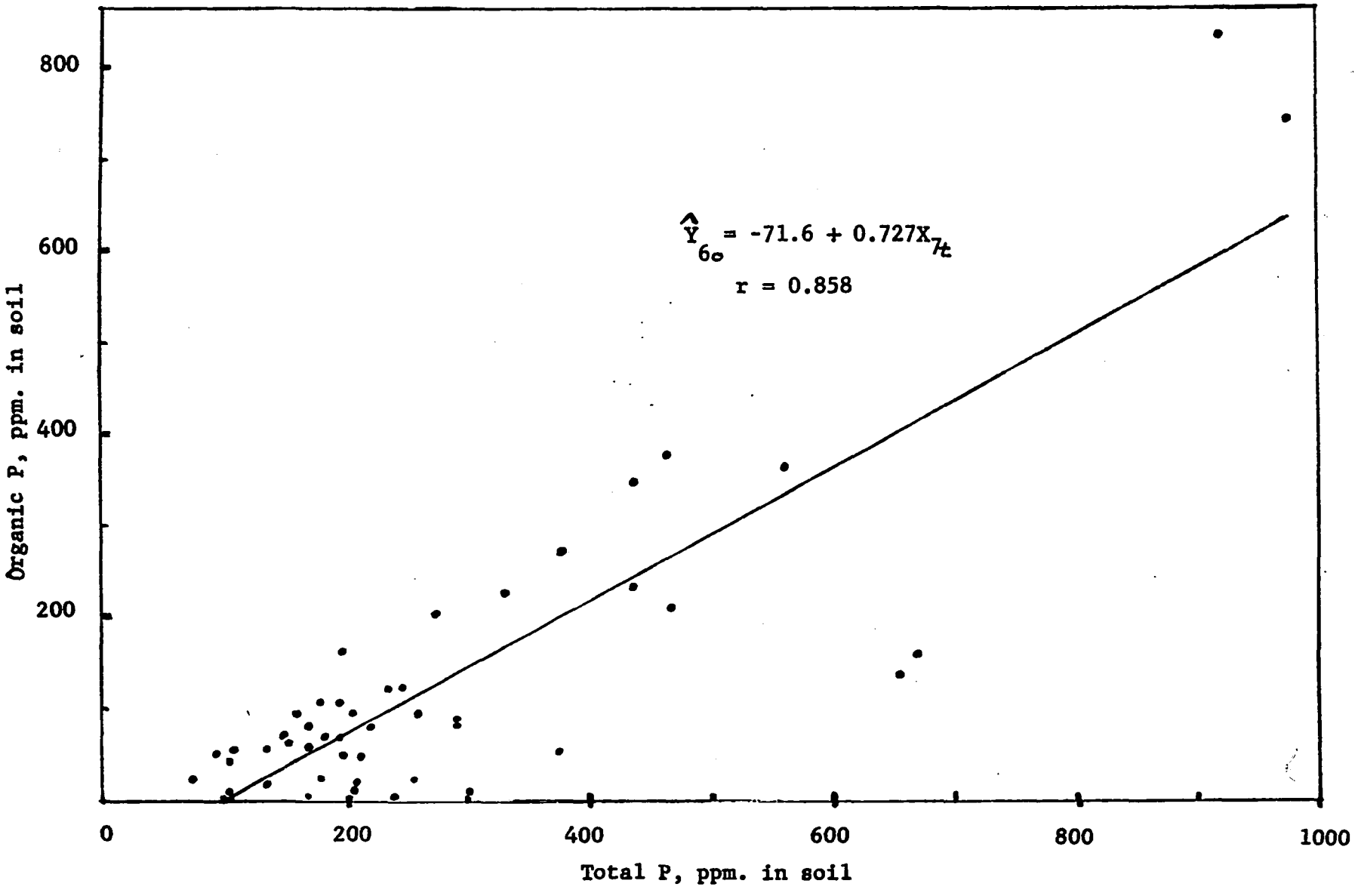

Figure 1- Relation between Organic P and Total P.

(a) $\hat{Y}_1 = -2.76 + 0.619X_1 - 0.0398X_2 + 0.0832X_3 \quad 0.0125X_4 + 0.260X_5 +$

$0.790X_6 - 0.203X_7$ - (I)

$R^2 = 0.907$: t values (in the same order as the X variables)

11.38^{**} [1/] -1.03 1.03 0.205 0.757

0.695 -1.39

(b) When factor X_9 was dropped:

$\hat{Y}_1 = 1.684 + 0.618X_1 - 0.44X_2 + 0.101X_3 + 0.0132X_4 + 0.216X_5 -$

$0.183X_7$ - (II)

$R^2 = 0.906$:

t values:

11.4^{**} -1.15 1.34 0.22 0.64

-1.28

(c) Factor X_{10} dropped:

$\hat{Y}_1 = 1.42 + 0.617X_1 - 0.0434X_2 + 0.093X_3 + 0.037X_4 - 0.139X_5$ - - -(III)

$R^2 = 0.905$: t values:

11.5^{**} -1.15 1.25 0.76 -1.12

(d) Factor X_5 dropped:

$\hat{Y}_1 = -0.84 + 0.637X_1 - 0.036X_2 + 0.075X_3 + 0.021X_4$ - - - - - - - (IV)

$R^2 = 0.902$: t values:

12.6^{**} -0.96 1.03 0.45

1/ ** Refers to a significant probability level of 1.0 per cent or less.

* Refers to a significant probability level of 5.0 per cent.

(e) Factor X_4 dropped:

$$\hat{Y}_1 = -0.38 + 0.640X_1 - 0.036X_2 + 0.093X_3 \quad \text{(V)}$$

$R^2 = 0.902$: t values:

12.9^{**} -0.99 1.56

(f) Factor X_3 dropped:

$$\hat{Y}_1 = 0.37 + 0.628X_1 - 0.003X_2 \quad \text{(VI)}$$

$R^2 = 0.896$: t values:

12.6^{**} -0.10

(g) Simple correlation:

$$\hat{Y}_1 = 0.24 + 0.625X_1 \quad \text{(VII)}$$

$r^2 = 0.896$ t value:

19.7^{**}

The relation between $NaHCO_3$-extractable P and the NH_4F-soluble P is presented in Figure 2. The change in the $NaHCO_3$-extractable P depends for 89.6 per cent on the NH_4F-soluble P when only this factor is considered. The negative simple correlation between this extractant and the clay factor indicated that higher the clay content, other factors being equal, the lower the $NaHCO_3$-extractable P.

In the previous regression equations the R^2 values, when different X factors were removed, decreased from 0.91 to 0.90. In all cases the coefficients of X_1 only were highly significant. It is considered that most of the variation in the extraction of P by the $NaHCO_3$ solution depends on the X_1 factor or Al-P form present in these soils.

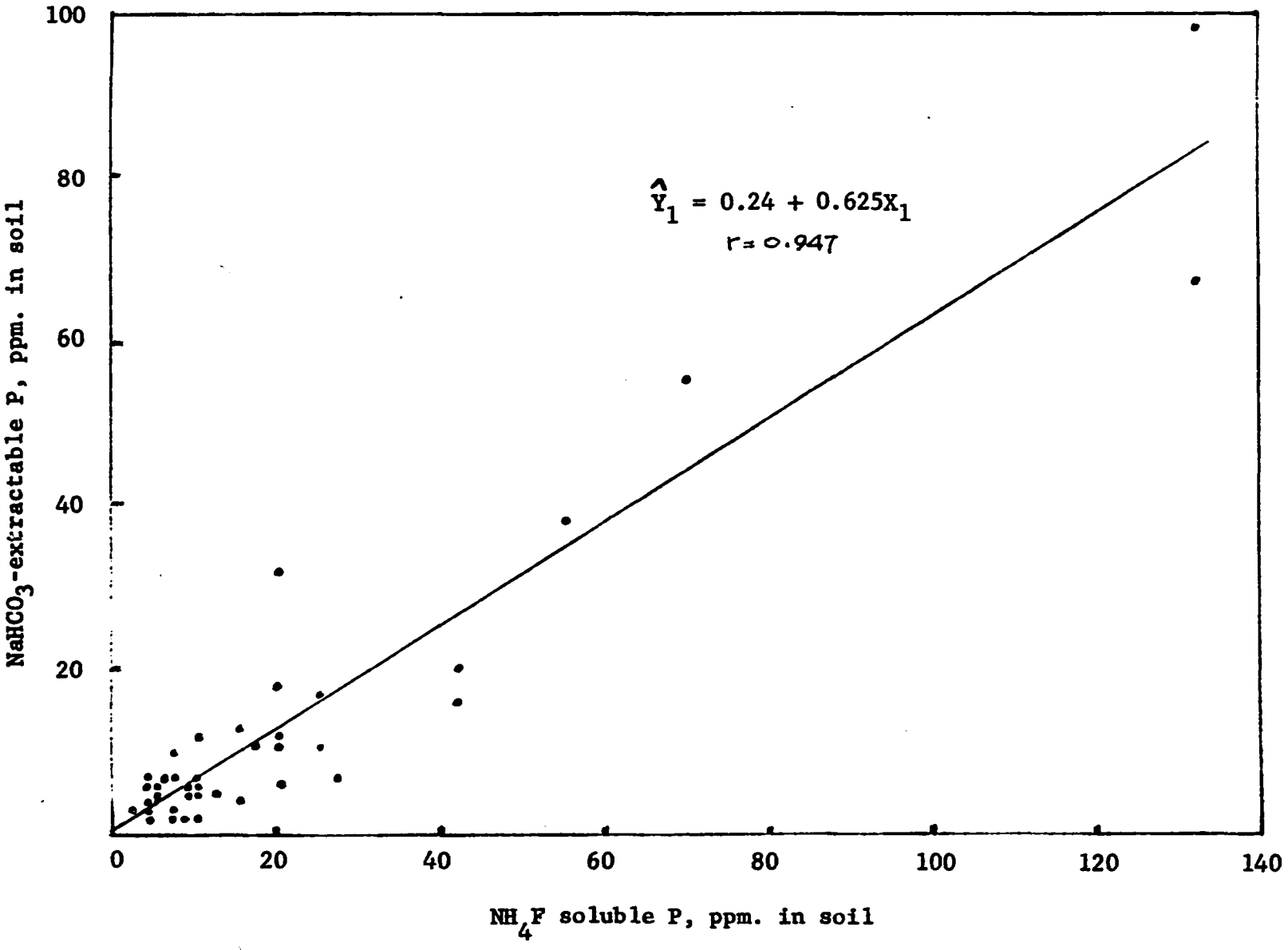

Figure 2- Relation between $NaHCO_3$-extractable P and NH_4F-soluble P.

In a multiple correlation analysis of the ammonium acetate-extractable P as a function of X_1 through X_7 and with the selective deletion of the X variables the equations were found to be:

(a) $\hat{Y}_2 = -1.99 + 0.214X_1 - 0.0159X_2 + 0.00735X_3 - 0.00458X_4 - 0.0410X_5 + 0.681X_6 - 0.0554X_7$ - - - - - - - - - - - - - - - - - - (VIII)

$R^2 = 0.896$: t values (in the same order as the X variables)

11.5**	-1.20	0.266	-0.219	0.349
1.75	-1.11			

(b) Factor X_9 removed:

$\hat{Y}_2 = 1.84 + 0.213X_1 - 0.0195X_2 + 0.023X_3 - 0.0040X_4 - 0.079X_5 - 0.038X_7$ - (IX)

$R^2 = 0.888$: t values:

11.2**	-1.45	0.86	-0.19	-0.67
-0.75				

(c) Factor X_{10} dropped:

$\hat{Y}_2 = 1.94 + 0.214X_1 - 0.020X_2 + 0.026X_3 - 0.013X_4 - 0.054X_5$ - - - (X)

$R^2 = 0.887$: t values:

11.3**	-1.47	1.00	-0.74	-1.22

(d) Factor X_5 dropped:

$\hat{Y}_2 = 1.07 + 0.222X_1 - 0.017X_2 + 0.0193X_3 - 0.019X_4$ - - - - - - - (XI)

$R^2 = 0.883$: t values:

11.3**	-1.26	0.76	-1.16

(e) Factor X_4 dropped:

$$\hat{Y}_2 = 0.65 + 0.219X_1 - 0.016X_2 + 0.003X_3 \text{ - - - - - - - - - - - - - (XII)}$$

$R^2 = 0.879$: t values:

12.2^{**} -1.21 0.14

(f) Factor X_3 dropped:

$$\hat{Y}_2 = 0.67 + 0.218X_1 - 0.015X_2 \text{ - - - - - - - - - - - - - - - - - (XIII)}$$

$R^2 = 0.879$: t values:

12.5^{**} -1.40

(g) Factor X_2 dropped:

$$\hat{Y}_2 = 0.25 + 0.199X_1 \text{ - (XIV)}$$

$r^2 = 0.873$: t value:

17.6^{***} (at 0.001 level of probability).

The relation between Ammonium acetate-extractable P and the NH_4F-soluble P is presented in Figure 3. Of the variation in the extraction of P by the Ammonium acetate, 87 per cent was explained by the NH_4F soluble P when this is considered alone. The negative correlation coefficient of the clay (Table IV) made evident that the lower the clay content, other factors being equal, the higher the ammonium acetate-extractable P.

The R^2 values in equations (VIII) to (XIV) decreased from 0.90 to 0.87. In the multiple correlation analysis with seven variables the pH factor gave a significant t value at the 0.100 level of probability. It is assumed that when pH is high more P is extracted but dropping this variable reduced the R^2 very little (0.90 to 0.89). All the t values for

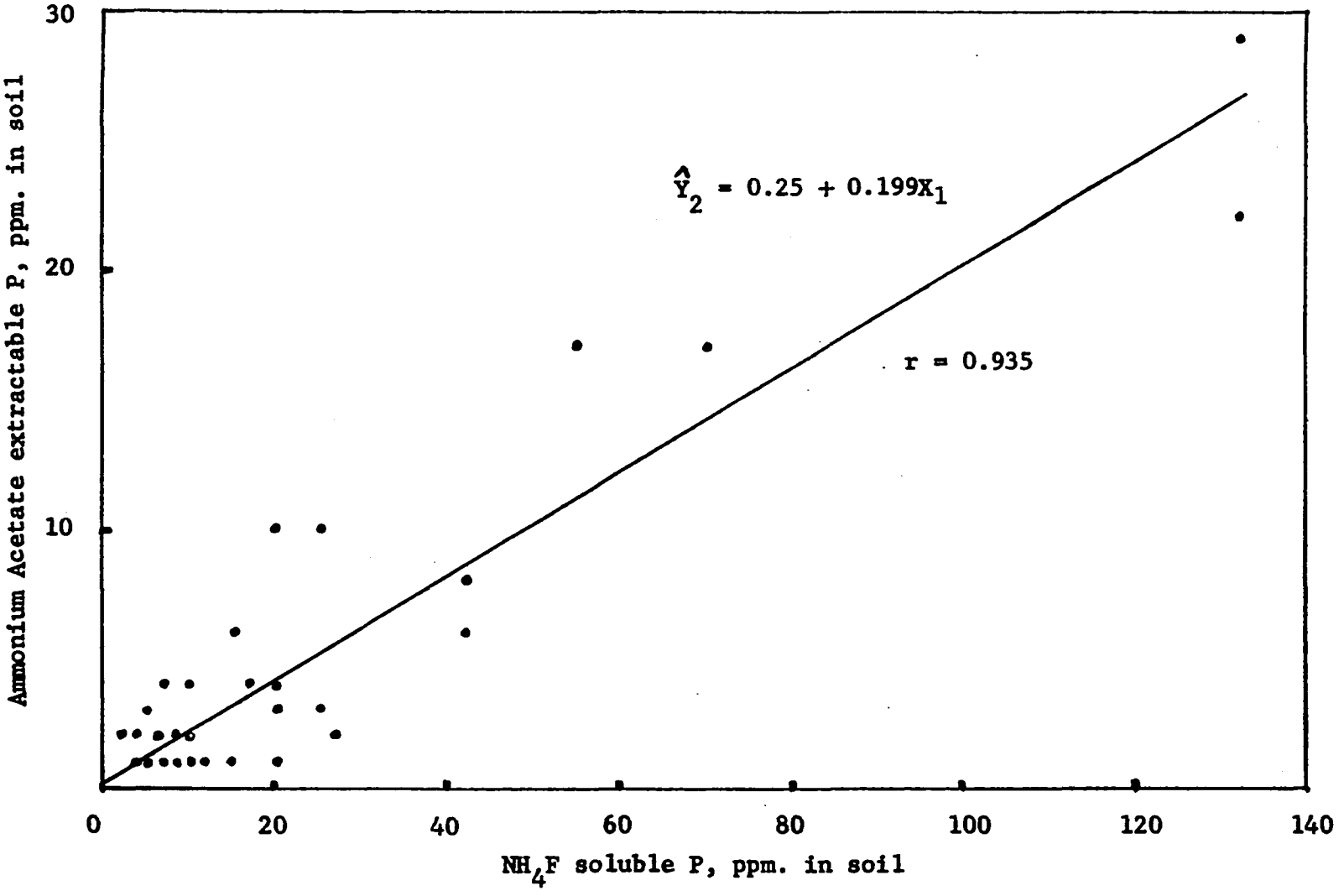

Figure 3- Relation between Ammonium Acetate-extractable P and NH_4F-soluble P.

the coefficient of X_1 were highly significant. Therefore most of the variation in the extraction of P by the Ammonium acetate is dependent on the Al-P form present in these soils.

The Bray-extractable P was also correlated positively with the N NH_4F-soluble, H_2SO_4 soluble, and Na-citrate soluble P and negatively with clay content, but in this latter case the significance is only at the 5.0 per cent level of probability.

When the factors considered were subjected to a multiple regression analysis with seven X_s and when removing the effect of each of the variables with lower association the equations were found to be:

(a) $\hat{Y}_3 = 56.45 + 1.84X_1 - 0.0212X_2 + 0.257X_3 + 0.123X_4 - 0.881X_5 - 7.79X_6 - 0.0296X_7$ - - - - - - - - - - - - - - - - - - (XV)

$R^2 = 0.947$:

t values:

14.69^{***} -0.237 1.38 0.875 -1.12

2.977^{**} -0.0879

(b) Factor X_9 dropped:

$\hat{Y}_3 = 12.64 + 1.83X_1 - 0.062X_2 + 0.44X_3 + 0.13X_4 - 1.32X_5 + 0.173X_7$ - (XVI)

$R^2 = 0.935$:

t values:

13.4^{**} -0.64 2.27 0.84 -1.55

0.48

(c) Factor X_{10} dropped:

$\hat{Y}_3 = 11.0 + 1.84X_1 - 0.065X_2 + 0.492X_3 - 0.14X_4 - 0.94X_5$ - - - (XVII)

$R^2 = 0.931$:

t values:

13.2^{**} -0.66 2.55^{**} -0.11 -0.29

(d) Factor X_5 dropped:

$$\hat{Y}_3 = -12.54 + 1.85X_1 - 0.060X_2 + 0.478X_3 - 0.025X_4 \text{ - - - - - (XVIII)}$$

$R^2 = 0.931$: t values:

14.3^{*} -0.62 2.57^{*} -0.21

(e) Factor X_4 dropped:

$$\hat{Y}_3 = -13.09 + 1.85X_1 - 0.059X_2 + 0.456X_3 \text{ - - - - - - - - - - (XIX)}$$

$R^2 = 0.931$: t values:

14.6^{**} -0.62 2.98^{**}

(f) Factor X_3 dropped:

$$\hat{Y}_3 = -0.42 + 1.79X_1 + 0.105X_2 \text{ - - - - - - - - - - - - - - - - - (XX)}$$

$R^2 = 0.917$: t values:

13.1^{**} 1.26

(g) Factor X_2 dropped:

$$\hat{Y}_3 = -6.8 + 1.92X_1 \text{ - (XXI)}$$

$r^2 = 0.914$: t value:

21.8^{***}

The relation between Bray-extractable P and NH_4F-soluble P is presented in Figure 4. As with the other two extractants more P is obtained when the contents of clay becomes lower. Two other aspects are observed here: (a) the pH factor in equation (XV) had a coefficient highly significant. Therefore the Bray-soluble P is dependent on the Al-P present in the soil and on the pH. The higher the pH the more P is extracted; (b) the factor Ca-P becomes significant when the pH

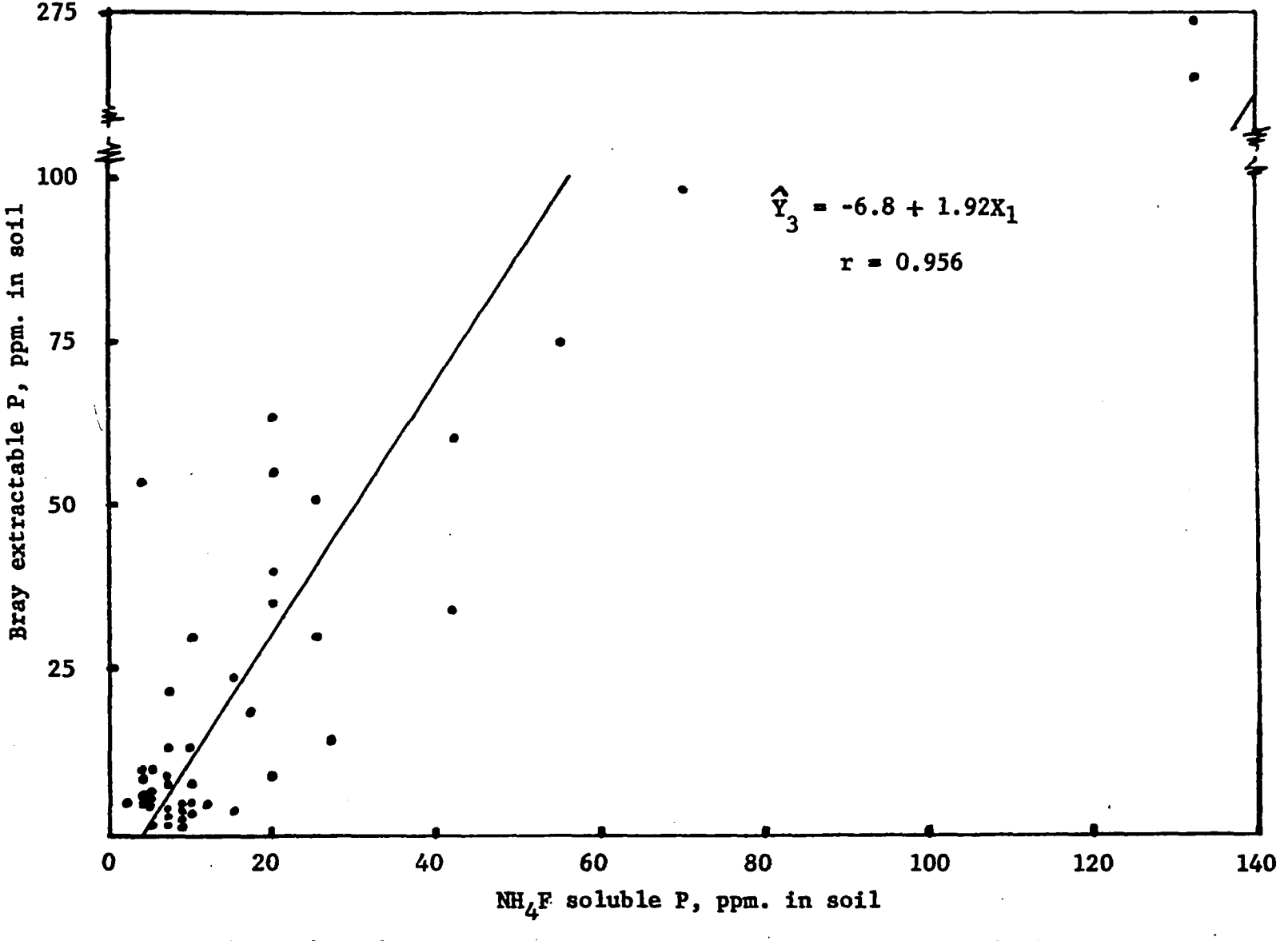

Figure 4- Relation between Bray-extractable P and NH_4F-soluble P.

component, clay percentage, and occluded Al-P factors, are removed separately. In this case again, the Bray-extractable P increases with higher Al-P and with higher Ca-P present in the soil. The coefficient of X_3 in equation (XIX) becomes highly significant, but the most decisive factor in the behavior of the extractable P by this buffered solution is still the Al-P form.

The effect of the independent variables Al-P and Ca-P on the Bray-extractable P was measured by correlating these factors and the results were:

$$\hat{Y}_3 = -13.60 + 1.793X_1 + 0.4005X_3 \text{ - - - - - - - - - - - - - - - -(XXII)}$$

$R^2 = 0.930$: t values:

20.0^{**} 3.25^{**}

with both coefficients of the variables highly significant again, but the Al-P form remains as the most important factor.

The R^2 percentage in removing the specified variables decreases from 95 to 91. Such a variation is of course linked to the nature of the extracting solution.

DISCUSSION AND CONCLUSIONS

Numerous investigations show that the content of organic P in soils is correlated with the content of organic matter. This conclusion has been demonstrated by Black and Goring (13), by Thompson, Black, and Zoellner (97) and others. In this study similar results were obtained when the correlation was established between organic P and total N, a constituent of the organic matter. A positive correlation was also observed between organic P and total P. This is in accord with the findings of Jencks, Raese, and Reese (48 a), and other workers.

The amount of organic P in soils may vary widely, as shown by the work of Schollenberger (88), Dean (29), Williams (103), and Thompson, Black and Zoellner (97). The extreme values according to these investigators include figures for surface soils, from 18 to 1670 ppm of organic P, with the last figure found in peat soils. When expressed as a percentage of the total P such values ranged from 2.6 to 75 per cent. In this study most of the values were within this range.

It appears from the previous works and that of Dickman and DeTurk (30), and others that the organic matter in mineral soils contains N, and P in roughly the ratio 9:1 by weight, and that the ratio is wider in soils with a high content of organic matter. Such a relationship is close to that observed in the subsoil samples in this study but the ratio in the surface soils was about 17:1.

Other studies (12) show that the amount of organic P decreases gradually with depth as it is evident in these soils.

The results of this investigation furnish circumstantial evidence

for the significance of soil organic P in that organic P varied with N and because organic P constituted an appreciable portion of the total P in the soils studied.

Little relationship was found between organic P and "available" P, a result which is in agreement with Barrow (7). This might be expected because of the lack of a direct equilibrium between the organic and inorganic forms of P.

The stability of soil organic P to mineralization appears to decrease with increasing soil pH. Thompson, Black, and Zoellner (97) found that mineralization of soil organic P increased with increasing pH. This is in agreement with the negative correlation found between organic P and pH for these soils. Although the coefficient was significant the value was low. Black and Goring (12) have shown that organic P mineralization increases with temperature (25^{o} or 30^{o} C), one might expect more mineralization in the warm climate of Louisiana than in northern states.

With the different extracting solutions to obtain the "available" P, the Bray method gave higher values because it is a strongly acid solution with ammonium fluoride, thus removing the acid soluble forms and the adsorbed forms of phosphate.

The $NaHCO_3$ method removed lower amounts of P in these soils where acid conditions predominate, and it has been suggested (70) that the HCO_3^- ion in the solution at pH 8.5 probably removes only the adsorbed P forms.

The ammonium acetate extracting solution gave lower values than those obtained with the other two procedures. It is considered that in this acid solution the acetate radical is less effective than the F^- ion in removing the adsorbed P forms (17). However, when these methods were

correlated with the P fractions, high and positive simple correlation coefficients were obtained, except with the occluded Al-P form.

The most abundant P-fraction was the Fe-P followed by the Ca-P which predominates in the subsoils when compared with the Al-P form. The latter form was higher in amount in some of the surface soil horizons.

There were high degrees of correlation between P as determined by quick methods and identified P-fractions. However, as shown in Table IV, the degree of association was much less for the occluded forms. One might then conclude that the most important P fraction in controlling the P extracted by the three quick methods is the NH_4F-soluble P. This fraction, Al-P was linearly correlated with $NaHCO_3$-extractable P, Ammonium acetate-extractable P, and Bray-extractable P and was involved in all multiple correlations.

If the $NaHCO_3$, Ammonium acetate, and Bray tests are accepted as reliable estimates of available P, then the conclusion follows that the NH_4F-soluble P is the most important P fraction in controlling available P in these acid soils. The NH_4F-soluble P probably consists mainly of Al-phosphates of various types, with variscite probably the dominant compound. This point of view is supported by Lindsay, Peech, and Clark (59) who showed that the solubility of P in acid soils was nearly the same value expected to be in equilibrium with variscite.

The importance of the NH_4F-soluble P in the simple and multiple correlations, is shown by the high and positive r^2 and R^2 values, and the fact that the t values for the NH_4F-soluble P were always highly significant.

Multiple regression analysis relating $NaHCO_3$-and Ammonium acetate extractable P with the P-fractions showed that no other t values were

significant besides that pertaining to the coefficient of X_1 or NH_4F-soluble P. In the case of the Bray-extractable-P the coefficient for pH in equation (XV) was significant. From this it was concluded that with higher pH values more P was removed, which fact is related to the acidity of this extractant. However, when this variable (pH) was dropped in equations (XVI) to (XIX) the coefficient of Ca-P became highly significant. This was no doubt due to the intercorrelation of pH and Ca-P ($r = 0.284$).

Another important factor in controlling the P extracted by $NaHCO_3$, Ammonium acetate and Bray reagents was the clay content of the soil. It had a significant negative influence on P-extractable. This is in accordance with the findings of Pratt and Garber (78), who explain that the textural effect is one of secondary precipitation in the case of the $NaHCO_3$ reagent, and an increased exhaustation of the reagent with increased clay content in the case of Bray reagent.

According to the registered observations it would seem that there is no one method of determining available P which is completely applicable to all soils.

The results of the chemical analysis offer evidence which indicates that the soils investigated were heterogeneous with respect to soil P compounds.

SUMMARY

1. Phosphorus (P) fractions in selected soils of East Baton Rouge Parish were determined including total, inorganic and organic P, the chemical P forms in the inorganic P-fraction, and the "available" P extracted by three different reagents. Other soil properties considered were pH, total N, and clay content.
2. Simple and multiple linear correlations were established between and among data obtained.
3. Organic P varied in surface samples from 12 to 836 ppm and averaged 159 ppm. Subsoil samples were generally lower, ranging from 1 ppm to 117 ppm and averaging 38 ppm. As a percentage of total P, organic P ranged from 7.2 to 87 per cent in surface samples and averaged 54.2 per cent. The range in subsoil samples was from practically zero to 40 per cent with an average of 21 per cent.
4. Statistical correlations of organic P with total P and total N were highly significant (r^2 values 0.74 and 0.57 respectively). Correlation with pH was significant but only 9.4 per cent of the variation of the organic P was accounted for by pH.
5. Simple correlations between and among data for the "available" P tests, five inorganic P fractions, pH and clay content were conclusive in indicating that the NH_4F-soluble P (or Al-P) was the most important inorganic P fraction in estimating the extracted "available" P by the three reagents used ($NaHCO_3$, Ammonium acetate, and Bray-solutions). Their r^2 values were 0.90, 0.87, and 0.91 respectively.

6. The P extracted by $NaHCO_3$ was also positively correlated with NaOH-soluble (Fe-P), H_2SO_4-soluble (Ca-P), and occluded Fe-P giving highly significant r values. The occluded Al-P was positively correlated but the coefficient was not significant. Negative correlation was obtained with both pH and clay content. The magnitude of simple correlation coefficients decreased in the same order of the selective dissolution extractions.
7. The same general behavior was observed with the P extracted by the ammonium acetate pH 4.2 and by the Bray solutions. In general, the occluded Al-P and pH gave low correlation coefficients with all P fractions. However, the H_2SO_4-soluble P (Ca-P) was correlated positively with pH, the occluded Fe-P with occluded Al-P, and occluded Al-P with clay all at a highly significant level.
8. Increasing clay content decreased the effectiveness of the three reagents in extracting "available" P from soils.
9. Multiple correlation analysis was used to relate the three extractants for "available" P, five inorganic P fractions, pH and clay. When $NaHCO_3$ extractable P was estimated with the seven independent variables, the R^2 value was 0.91. When only NH_4F-soluble P was considered the value of r^2 was 0.90. With ammonium acetate the R^2 value was 0.90 with seven variables and dropped to 0.87 when only NH_4F-soluble P was considered. In the case of the Bray-P with the seven variables R^2 was 0.95. With the factors NH_4F-soluble P and H_2SO_4-soluble P, R^2 was 0.93 and with NH_4F-soluble P alone r^2 was 0.91.
10. The chemical analysis indicated that the soils studied were heterogeneous with respect to soil P compounds.

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VITA

B. Ortiz-Villanueva was born June 1, 1918, in Cuitzeo, Mich., Mexico. He was reared in Morelia, Mich., Mexico, where he attended public schools and received a high school diploma in December 1935. He entered Mexico Agricultural College, at Chapingo, Mexico in February, 1936, finishing those studies in November, 1942, and received a diploma as Agricultural Engineer, Specialist in Irrigation, in 1945 after presenting a Thesis on "Potable Water Supply. Agricultural Centers of Rural Population".

He worked with the Mexican Irrigation Department as an Edafologist from 1943 to 1947. In 1947 he received a scholarship from the French Government to study in the Institute of Agronomy in Paris for a period of two years following which he returned to his previous work in soil mapping. During 1950 and 1951 he was on a scholarship from the Bank of Mexico to study Soil Science in the United States, obtaining the M.S. degree from Louisiana State University. From 1951 through 1962 he has been working with the Mexican Sugar Industry as a soil technician and his activities have been mainly concerned with soil studies and experimental work with fertilizers applied to the sugar cane.

He is a member of the International Society of Sugar Cane Technologists, the Mexican Society of Agronomy, the Latin-American Society of Soil Science, and the Latin-American Society of Chemistry.

For short intervals he has worked and obtained technical information under the guidance of North American soil scientists. In 1953 he made observations on the sugar cane ripening program followed in a Panama plantation; later, he was a visitor in the N. C. State College,

at Raleigh, N. C., in the University of Illinois, Urbana, Illinois, and in the Regional Soil Salinity Laboratory in Riverside, California, with the purpose to introduce improvements in the soil testing laboratory of the Mexican Sugar Industry.

During 1955 he was a visitor in the Pan American Agricultural School in Turrialba, Costa Rica, and in the Imperial College of Tropical Agriculture in Saint Augustine, Trinidad, British West Indies. The same year he visited the Agricultural Experiment Station of Rio Piedras in Puerto Rico to be acquainted with the foliar analysis applied to sugar-cane in search of more balanced fertilizer recommendations. In 1956 he was in Hawaii to become familiar with the Croplog System of Clements to be applied to the sugar cane crop in Mexico.

He has written thirty technical papers dealing with Mexican soils and agricultural experimental results. In 1961 he was invited by the Chinese Government from Taiwan to make observations about the progress and results on the Land Reform and Agricultural Production Programs. A report was presented on this observation and it was widely distributed in all the Latin-American countries by the Free China Organization. In 1962 he worked as assistant in research in the University of California, Berkely, California. He is now a candidate for the degree of Doctor of Philosophy in the Department of Agronomy.

EXAMINATION AND THESIS REPORT

Candidate: Ortiz-Villanueva, Bonifacio

Major Field: Agronomy

Title of Thesis: Phosphorus Fractions in Soils of East Baton Rouge Parish

Approved:

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July 24, 1964